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Abstract

Mutual diffusion coefficients have been measured for aqueous $NaCl-SrCl_2$ mixtures at 25°C by using free diffusion Rayleigh interferometry. These diffusion experiments were done at total molarities of 0.5 and 1.0 mol•dm^{-3} and with molarity fractions of 1/3, 1/2, and 2/3. Main term diffusion coefficients for NaCl and $SrCl_2$ show a 10-15% variation with concentration and composition. Coupled diffusion is important for these systems, with cross term diffusion coefficients being 6.5-36% as large as their corresponding main terms. At a constant molarity ratio, doubling the concentration causes cross-term diffusion coefficients to increase. Attempts to estimate the ternary solution diffusion coefficients from those of their corresponding binary solutions or from the ternary solution analogues of the Nernst-Hartley equation do not yield particularly accurate results.

1. Introduction

Mutual diffusion coefficients of aqueous electrolytes are required for understanding and modeling a wide variety of chemical, geochemical, and industrial processes.[1,2] Mutual diffusion coefficients are also part of the input information required for calculation of the ionic Onsager ℓ_{ij} transport coefficients[3,4] and also velocity correlation coefficients.[5] These experimentally based ℓ_{ij} and vcc values are needed for comparison with and as a guide for theoretical calculations, and to test approximation methods.

A fair amount of accurate mutual diffusion data are available for binary aqueous metal chloride and sulfate solutions at 25°C. See references 6-10 and references cited by them. Data at other temperatures [11-14] are extremely limited. Data gaps are much more severe for ternary electrolyte solutions, since, in most cases, only a few compositions have been investigated and then only for a limited number of systems.

The greatest amount of ternary aqueous electrolyte diffusion data exists for mixtures of 1-1 electrolytes. Systems with accurate data are $NaCl$-KCl-H_2O with six compositions,[15-18] one composition each of $LiCl$-KCl-H_2O and $LiCl$-$NaCl$-H_2O,[19,20] four compositions of $(C_2H_5)_4NBr$-KBr-H_2O,[21] one composition of $(C_2H_5)_4NCl$-KCl-H_2O,[22] four compositions of Bu_4NBr-KBr-H_2O,[23] one composition of Bu_4NBr-HBr-H_2O,[24] one composition of KBr-HBr-H_2O,[25], thirteen compositions (all but two very dilute) of KCl-HCl-H_2O,[26,27] three compositions of $NaCl$-HCl-H_2O,[26] and four compositions of choline chloride-HCl-H_2O.[28] Data also exist for several compositions of mixtures of 1-1 electrolytes with weak acids, amino acids, or organic nonelectrolytes.[9,29-35]

Experimental data are even more scarce for ternary solutions involving one or more higher valence electrolytes. Eight compositions of Na_2SO_4-H_2SO_4-H_2O[36,37] have been studied using Gouy interferometry and conductometric measurements, as have eighteen compositions of H_3PO_4-$Ca(H_2PO_4)_2$-H_2O by Gouy interferometry.[38] Six dilute compositions of Na_2SO_3-$NaOH$-H_2O were also investigated using the conductometric method.[39]

Diffusion data for three compositions of $NaCl-MgCl_2-H_2O$ were reported using diaphragm cells;[40] however, such measurements yield integral diffusion coefficients that must be differentiated to yield the desired mutual diffusion coefficients. This differentiation produces large uncertainties and potentially serious errors in the calculated mutual diffusion coefficients. We have also reported mutual diffusion data for one composition each of $NaCl-MgCl_2-H_2O$ and $NaCl-Na_2SO_4-H_2O$.[2]

Mutual diffusion data for $Na_2SO_4-H_2SO_4-H_2O$ should be highly atypical owing both to strong ion-pairing and bisulfate ion formation.[36,37,41] Similar considerations apply to $H_3PO_4-Ca(H_2PO_4)_2-H_2O$. Thus, only very limited accurate diffusion data are available for mixtures involving higher valence strong electrolytes. Consequently, very little information is available for guiding the development of the theories of Onsager ℓ_{ij} and velocity correlation coefficients.

To provide some of the critically needed data for mixtures involving higher valence electrolytes, we began measuring mutual diffusion coefficients at Lawrence Livermore National Laboratory. Systems being systematically investigated are $NaCl-SrCl_2-H_2O$ (which has waste isolation applications), $NaCl-MgCl_2-H_2O$ (which has applications to seawater and concentrated brines), and $ZnCl_2-KCl-H_2O$ (which has applications to zinc-halogen batteries). Here we give diffusion data for six compositions of $NaCl-SrCl_2-H_2O$ with total molarities of 0.5 and 1.0 $mol \cdot dm^{-3}$ at 25°C by using Rayleigh interferometry. These measurements will later be extended to higher concentrations. Osmotic/activity coefficient data are also required for a detailed irreversible thermodynamics analysis of these systems; we have measured and reported isopiestic data for $NaCl-SrCl_2-H_2O$ and $NaCl-MgCl_2-H_2O$.[42,43]

It should be noted that two electrolytes <u>with</u> a common ion in an essentially non-ionized solvent such as H_2O form a ternary solution for diffusion. Two electrolytes <u>without</u> a common ion in H_2O form a quaternary solution for diffusion.

2. Experimental Measurements and Solutions

Our mutual diffusion coefficients were measured at 25.00±0.005°C using a modified Beckman-Spinco model-H electrophoresis apparatus operated as a free-diffusion Rayleigh interferometer. The optics of this apparatus were realigned and upgraded to improve and optimize the Rayleigh measurements.[7,44] All diffusion measurements were performed in a cell with walls of Ta-metal (which is quite inert to chemical attack) and windows of one cm thick optical glass.

The magnification factor MF of our optical apparatus was determined to be 1.005021±0.000037 by photographing a transparent ruled scale in the center-of-cell position, and then comparing the scale separation on the glass photographic plates to their corresponding separations on the original scale.[7] The measured optical constant $B=(4.125_5\pm0.000_3)\times10^{-5}$ $cm^2\cdot min\cdot mm^{-2}\cdot s^{-1}$, required for calculating the diffusion coefficients, depends on $(MF)^2$ so its relative uncertainty is twice as large as for MF.

Two concentrated $SrCl_2$ stock solutions were prepared by dissolving Baker analyzed "low in magnesium" $SrCl_2\cdot6H_2O(cr)$ in purified water followed by filtration. This water had been purified by deionization followed by distillation. Ternary solutions were then prepared by weight using samples of $SrCl_2$ stock solution, oven-dried NaCl (Mallinckrodt analytical reagent or Baker analyzed), and H_2O. All weights in this study were converted to weights in vacuo. Direct current arc optical emission spectroscopy of the original $SrCl_2\cdot6H_2O$ for impurities indicated 30 ppm Ca, 50 ppm Ba, 10 ppm Al, 2 ppm Fe, and $\leq$10 ppm each Mg and Si by weight.

The concentrations of our $SrCl_2$ stock solutions were determined both by dehydration of samples to constant weight at 230-300°C, and by conversion to the anhydrous sulfate at 410-550°C. Triplicate samples were used in each case. Stock solution #1 had a concentration of 3.1721±0.0007 $mol\cdot kg^{-1}$ by dehydration and 3.1728±0.0007 by conversion to sulfate; stock #2 had a concentration of 3.3669±0.0008 $mol\cdot kg^{-1}$ by dehydration and 3.3676±0.0011 by conversion to sulfate. These uncertainty limits are mean deviations. Mean analyses were used for calculating ternary solution concentrations. Assumed molecular masses are 158.526 $g \cdot mol^{-1}$ for $SrCl_2$, 183.678 $g \cdot mol^{-1}$ for $SrSO_4$, 58.443 $g \cdot mol^{-1}$ for NaCl, and 18.0152 $g \cdot mol^{-1}$ for H_2O.

Details of the cell filling and diffusion measurements are given elsewhere.[7] Concentration gradients were kept small enough that the calculated diffusion coefficients are on the volume fixed reference frame and are <u>differential</u> diffusion coefficients.[9]

Our solutions were prepared by mass, so their concentrations are known on the molal scale. However, Fick's laws apply to the molarity (volumetric) concentration scale, so densities are needed to perform this conversion. They were measured to $2\text{-}3 \times 10^{-5}$ $g \cdot cm^{-3}$ at 25.00±0.005°C by using two ≈31 cm^3 single stem pycnometers that had been calibrated 7 or 9 times by using purified water. Details of the procedure are given elsewhere.[45]

Densities were measured for all of the solutions used in our diffusion experiments, and for 1-3 other compositions close to each mean molarity composition. These density data at each of the six overall compositions were represented by the Taylor series expansion[46]

$$d = d^* + H_1(c_1 - c_1^*) + H_2(c_2 - c_2^*) \tag{1}$$

where d is the density in $g \cdot dm^{-3}$, c_i the molarity of salt i in $mol \cdot dm^{-3}$, 1 denotes NaCl, and 2 denotes $SrCl_2$. The expansion concentrations c_i^* were fixed by making $c_1^* + c_2^* = 0.5$ or 1.0 $mol \cdot dm^{-3}$ exactly, and these c_i^* were very close to the actual overall mean experimental molarities $\bar{\bar{c}}_i$ for each overall composition.

Table I contains the observed parameters for eq. 1, and the standard deviation of the density $\sigma(d)$ for that fit. The actual experimental densities will be published elsewhere, along with data at other concentrations.[47] Also given in Table I are the partial molal volumes $\bar{V}_i$ in $cm^3 \cdot mol^{-1}$. The solvent is denoted by 0. These density values are needed for conversions of concentration scales, for diffusion coefficient reference frame transformations,[3-5,9,10,48] and for tests of the static and dynamic stability of the solutions undergoing diffusion.[49]

Tables II-VII contain the individual concentration data for each diffusion experiment. Values of $\bar{c}_i$ are the average molarity concentrations for a single diffusion experiment, and the Δc_i are the concentration differences of salt component i across the initial boundary. Four or five different diffusion experiments were performed for each overall composition at nearly identical $\bar{c}_1, \bar{c}_2$ but with different Δc_i. Experiments were generally performed with either Δc_1 or $\Delta c_2 \approx 0$ (and the other $\Delta c_i > 0$), and for two or three intermediate concentration differences (Δc_1, $\Delta c_2 > 0$). The Δc_i values were fixed so as to have about 80-90 Rayleigh fringes in each experiment.

Each diffusion pair in Tables II-VII is initially density stable, but the possibility existed that it could become statically or dynamically unstable during diffusion. Calculations using the detailed theory for convective instabilities[49] indicates all of our chosen Δc_i ratios were stable. In fact, all cases with $\Delta c_1 \geq 0$ and $\Delta c_2 \geq 0$ are stable at the six overall compositions used in this study.

3. Calculation of Diffusion Coefficients

The positions of the Rayleigh fringes on the photographic plates were determined to 1-2 microns using a Grant comparator. Diffusion coefficients were then calculated using symmetrical "Creeth" pairing of fringes.[50] This type of fringe pairing cancels out the largest optical aberrations[51] (including the Wiener skewness which would otherwise remain for a center-of-cell focus),[44] and also most of the effects of the concentration dependence of the diffusion coefficients between the top and bottom solutions of the diffusion pair.[52] Fringe position data were baseline corrected for minor imperfections in the optical flats forming the front and back of our cell as well as other optical components of the system.

The fringe pairs used in calculating our diffusion coefficients were determined by using the fixed cut-off criteria given by $0.28 \leq |f(j)| \leq 0.84$. Here, f(j) is the reduced fringe number defined by

$$f(j) = \frac{2j-J}{J} \tag{2}$$

where j is the number of an individual fringe and J is the total number of fringes. The higher cut-off criterion eliminates the outermost fringes of the diffusion pattern which are broader and more strongly sloped, and, therefore, harder to center accurately.[2,14]
The lower cut-off eliminates the inner fringes whose separations are too small to allow precise f(j) values to be determined.

By using fixed cut-offs for f(j), a consistent calculation can be made of the Δt time correction for skewed fringe patterns from each diffusion experiment.[2] Each Δt value is the sum of two separate factors: (1) the initial diffusion boundary is not the ideal case of being a step-function of concentration; its finite width corresponds to an effective time it would take for an infinitely sharp boundary to diffuse to the actual initial boundary width; (2) there is also a slight time delay between when the siphoning needle is raised and the reservoir stopcocks closed, and when the timing clock is started. The sum of these two terms, Δt, is obtained by plotting the apparent diffusion coefficient D' against 1/t'. Here t' is the apparent or clock time, and it is equal to $t-\Delta t$ where t is the "true time" for diffusion from an infinitely sharp boundary. The D' vs. t' plot is a straight line and its slope yields Δt. Its intercept, the apparent diffusion coefficient extrapolated to infinite time, would be the "true" diffusion coefficient D for a binary solution. In a multicomponent mixture, it is the pseudo-binary D.

For a series of diffusion experiments at the same overall composition, the total number of Rayleigh fringes can be represented by

$$J = R_1 \Delta c_1 + R_2 \Delta c_2 \tag{3}$$

where the R_i are refractive index increments. These R_i values are obtained by least-squaring values of J as a function of the initial Δc_i for all the experiments with the same overall composition. Also of interest are the fractional refractive index contribution of each electrolyte to the total number of fringes

$$\alpha_i = R_i \Delta c_i / J \tag{4}$$

Diffusion in a ternary solution is governed by Fick's First Law

$$-J_1 = D_{11}\left(\frac{\partial c_1}{\partial x}\right) + D_{12}\left(\frac{\partial c_2}{\partial x}\right) \tag{5}$$

and

$$-J_2 = D_{21}\left(\frac{\partial c_1}{\partial x}\right) + D_{22}\left(\frac{\partial c_2}{\partial x}\right) \tag{6}$$

where J_i is the flow of electrolyte i, c_i the molar concentration of electrolyte i, the D_{ij} are the four ternary diffusion coefficients in $cm^2 \cdot s^{-1}$, and x is the vertical distance downward from the center of the boundary.[4] D_{11} and D_{22} represent the diffusion coefficients of electrolytes 1 and 2, respectively, each due to its own concentration gradient. Cross-term diffusion coefficients, D_{12} and D_{21}, arise from coupled flow of one electrolyte caused by the gradient of the other electrolyte.

For Rayleigh interferometry with the free-diffusion boundary conditions used in our experiments, the reduced fringe number is given by[53,54]

$$f(j) = (a+b\alpha_1)\ \mathrm{erf}(s_+ y_j) + (1-a-b\alpha_1)\ \mathrm{erf}(s_- y_j) \tag{7}$$

Here y_j is the reduced position of an individual fringe, defined by

$$y_j = x_j/(2t^{1/2}) \tag{8}$$

where x_j is the distance in cm of fringe j from the center of the boundary at time t.

The quantities s_+ and s_- are functions of the D_{ij}, whereas a and b are functions both of D_{ij} and R_i. Consequently, the D_{ij} can be back-calculated from a, b, s_+, s_-, R_1 and R_2.[53]

Equation 7 is non-linear in terms of the experimental variables j, J, x_j, and t, as well as the derived quantities a, b, s_+, and s_-. It can be fitted to the experimental variables by a standard iterative least-squares procedure, based on its Taylor series expansion with respect to a, b, s_+, and s_-. If these variables are denoted by g_i, then

$$f(j) = f(j)^\circ + \sum_{i=1}^{4} \left(\frac{\partial f(j)}{\partial g_i}\right)^\circ \Delta g_i \tag{9}$$

where the super "°" refers to that particular function evaluated at some chosen initial values for the least-squares variables. In the majority of cases (including the six compositions of $NaCl-SrCl_2-H_2O$ reported here), suitable initial values of a, b, s_+, and s_- are 0, 1, $D_1^{-1/2}$, and $D_2^{-1/2}$, respectively. Here, D_1 is the pseudo-binary diffusion coefficient of a diffusion pair with $\Delta c_2=0$, and D_2 is the pseudo-binary diffusion coefficient of a diffusion pair with $\Delta c_1=0$.

Least-squaring the various fringe positions for two or more diffusion experiments with the same overall average composition gives Δg_i. New "initial" values $(g_i+\Delta g_i)$ are substituted into equation 9, and the procedure repeated to obtain new Δg_i. These iterations continue until all $\Delta g_i \leq 0.0001$. This non-linear least-squares procedure usually converges in 3-7 iterations. A 2σ rejection criteria was used for individual f(j) points.[2] Baseline corrections were made. Although, in principle, two experiments would be sufficient to characterize all four least-squares variables, we did 4-5 diffusion experiments for each overall average composition in order to improve the statistics of the calculations, to verify that there were no instabilities for any of our $\Delta c_1/\Delta c_2$ ratios, and to locate and eliminate an occasional inaccurate experiment.

Tables II-VII contain the concentration information for sets of experiments performed at each overall average composition. Also given are the starting time corrections Δt, the experimental J values, and least-squares values of J from eq. 3. Tables VIII and IX give the resulting volume fixed diffusion coefficients D_{ij} along with their standard 1σ errors, values of R_i, values of s_+ and s_-, and values of $m_i(\bar{\bar{c}}_1,\bar{\bar{c}}_2)$ which are the average molalities corresponding to the average molarities $\bar{\bar{c}}_1$ and $\bar{\bar{c}}_2$.

These $m_i(\bar{\bar{c}}_1,\bar{\bar{c}}_2)$ values are needed for calculation of activity derivatives for a detailed irreversible thermodynamics analysis of diffusion data, since the activity coefficient equations are all on the molal concentration scale.[42,43] Also given in Tables VIII and IX are the calculated solvent-fixed diffusion coefficients D^o_{ij}; values on this reference frame are more readily amenable to an irreversible thermodynamics analysis.[4]

Tables VIII and IX also contain values of S_A which was defined by Fujita and Gosting.[55] S_A depends on the D_{ij}, R_1, and R_2. Systems with $|S_A|<15$ have increasingly large uncertainties for D_{ij}; rather larger values of S_A as found here are conducive to more accurate extraction of the four D_{ij}.

The results in Tables VIII and IX show coupled diffusion is important for these systems. Cross terms vary from 6.5-36% of their corresponding main terms.

4. Discussion of Results

Figures 1-3 show the D_{ij} values for $NaCl$-$SrCl_2$-H_2O at constant total molarity ($\bar{\bar{c}}_1+\bar{\bar{c}}_2$ = 0, 0.5, and 1.0 $mol{\cdot}dm^{-3}$, respectively) as a function of the molarity fraction of NaCl in these solutions. Values at infinite dilution, i.e, $\bar{\bar{c}}_1+\bar{\bar{c}}_2=0$, were calculated from the ternary solution analogues of the Nernst-Hartley equation.[4] These diffusion coefficients at infinite dilution can be calculated exactly, using only the limiting ionic electrical conductances[56] and certain fundamental constants. Only the qualitative features of the infinite dilution curves are retained at our higher concentrations of 0.5 and 1.0 $mol{\cdot}dm^{-3}$. Particularly noteworthy is that the Nernst-Hartley analogue ternary solution equations predict that D_{12} will become very large as $\bar{\bar{c}}_1/(\bar{\bar{c}}_1+\bar{\bar{c}}_2)\rightarrow 1$, and this has been amply confirmed by our experiments.

At higher concentrations we do not know all of the D_{ij} over the full concentration range, but only over the actual experimental concentration range. However, two of the diffusion coefficients D_{ij} can be obtained at each end of the composition range. Let $w_i=\bar{\bar{c}}_i/(\bar{\bar{c}}_1+\bar{\bar{c}}_2)$. Then, as $w_1\rightarrow 1$, D_{11} becomes equal to its pure binary solution term evaluated at the total molarity, and D_{21} goes to zero since there is no solute 2 to be transported by salt 1.[10,15] However, D_{12} approaches a large finite value as w_1=1 and D_{22} becomes equal to the trace diffusion coefficient of cation 2 under these conditions. Similarly, as w_2->1, D_{22} becomes equal to its corresponding binary term, D_{12} goes to zero since there is no solute 1 to be transported by salt 2, and D_{11} becomes equal to the trace diffusion coefficient of cation 1. The virtually identical values of D_{11} and D_{22} at $\bar{\bar{c}}_1+\bar{\bar{c}}_2$=0 and w_1=0 are fortuitous for this system.

Experimental values of D_{ij} are very smooth functions of w_i at constant $\bar{\bar{c}}_1+\bar{\bar{c}}_2$, figures 2 and 3. However, D_{12} either shows a small amount of scatter or exhibits a more complicated, s-shaped concentration dependence not present for the other three D_{ij}.

We cannot obtain D_{22} and D_{12} as w_1->1, or D_{11} and D_{21} as w_1->0, at finite total concentrations either from the present data alone or from theory. To characterize their behavior in these composition regions would require a number of additional and time consuming experiments. The infinitely dilute solution prediction that D_{22} and D_{12} cross as w_1 approaches 1, figure 1, also may occur at the higher concentrations. It appears to be nearly true, as indicated by a rough extrapolation of experimental trends outside our present experimental concentration range.

The experimental D_{ij} values in Tables VIII and IX also contain their corresponding standard errors σ. One thing should be noted about these σ values: at constant $\bar{\bar{c}}_1+\bar{\bar{c}}_2$, as w_1->0 the σ values generally increase significantly, especially for the main term coefficients D_{11} and D_{22}. A main factor causing this is as follows. Four distinct coefficients D_{ij} need to be extracted from a series of 4-5 experiments with various $\Delta c_1/\Delta c_2$ ratios but nearly identical $\bar{c}_1$ and $\bar{c}_2$. If D_{11} and D_{22} show significant differences in numerical values, and one or both of the cross term coefficients are small, then the four diffusion coefficients can easily and accurately be extracted. However, if D_{11} and D_{22} are close in value, especially if one or both cross term coefficients are small, then the system behaves almost like a binary solution during diffusion. Thus, trying to extract four correlated coefficients from these experiments becomes more difficult and the uncertainties become much larger. A more exact way of stating this is that the uncertainties increase as the eigenvalues of the diffusion matrix, $1/s_+^2$ and $1/s_-^2$, approach each other.

Doubling the total concentration from $\bar{\bar{c}}_1+\bar{\bar{c}}_2=0.5$ to 1.0 $mol \cdot dm^{-3}$ caused a significant increase in D_{12} and D_{21} at all molarity fractions, and a significant decrease in D_{11}; much smaller effects occur for D_{22}. At a constant total molarity, increasing w_i causes both main and cross term coefficients to increase regularly for salt i, whereas those for the other salt decrease as w_i increases. Obviously, if we look instead at the other salt (denoted by j), then the above also holds true as $w_j \to 1$.

5. Estimation Methods

The most accurate experimental methods for determination of mutual diffusion coefficients at low to high concentrations are optical interferometry (mainly Rayleigh and Gouy optics),[9,10] and, at low to very low concentrations, is Harned's conductometric method.[27,39,56] Diaphragm cell measurements, which are usually done with large concentration gradients, can yield precise integral diffusion coefficients. However, these integral diffusion data must then be differentiated to yield the desired mutual diffusion coefficients. For binary solutions under very favorable conditions of concentration dependence, errors for mutual diffusion coefficients from diaphragm cell measurements are several times larger than for optical measurements. For unfavorable concentration dependences, the diaphragm cell values have errors 10-100 times as large.[6,14] It is clear that diaphragm cell measurements for ternary and higher order systems are usually of questionable value at present. Modifications of the diaphragm cell method, using much smaller concentration gradients, are currently being developed and may significantly improve the accuracy of derived diffusion coefficients for that method.[57]

Diffusion measurements using optical interferometry involve much painstaking and tedious experimental work. Consequently, few experimental groups do such measurements, so relatively little reliable ternary solution diffusion data are available, as noted in the Introduction. It is thus highly desirable to try to develop reliable approximation methods to estimate multicomponent diffusion coefficients. Obvious starting points for such methods are the corresponding binary solution diffusion coefficients, Onsager ℓ_{ij} transport coefficients, or ionic parameters such as the limiting ionic conductances.

One estimation approach is to equate the main term diffusion coefficients to their corresponding binary solution diffusion coefficients at some kind of comparable concentration. That involves setting cross term diffusion coefficients equal to zero. This is a major deficiency of that approach, because as we have seen, Tables VIII and IX and figures 1-3 show large cross term diffusion coefficients at certain overall concentrations and salt ratios.

There are obviously many "comparable concentrations" which could be used to estimate the main term diffusion coefficients from their corresponding binary solutions. Examples are constant total molarity, constant volumetric ionic strength, constant volumetric equivalents, constant total molality, constant molal ionic strength, etc. In this paper we will only consider constant volumetric ionic strength. After we have reported additional data for other concentrations, we will test cross-plotting these results on different concentration scales to determine which one yields the more accurate mixing rule.

A second approximation method is to use the ternary solution analogue of the Nernst-Hartley equation, which is based on limiting ionic electrical conductances.[4] It is completely accurate at infinite dilution. As seen in figures 1-3, it also seems to give fair qualitative predictions at higher concentrations. However, at constant w_i, it incorrectly predicts that D_{ij} do not depend on total concentration whereas they do as shown in Tables VIII and IX. It is possible to modify this equation using other terms such as activity coefficient terms or relative viscosities to partially compensate for the observed concentration dependences. Owing to the non-rigorous introduction of these terms, we will only use the simple Nernst-Hartley limiting equations for D_{ij} here.

In a third approach, Miller described several methods for estimating D_{ij} for 1-1 electrolyte mixtures from binary solution data using the solvent-fixed generalized Onsager transport coefficients ℓ_{ij}.[4] However, as indicated by equations 36-4[illegible] of reference 4, to calculate these ℓ_{ij} requires solvent-fixed thermodynamic diffusion coefficients

L^{o}_{ij}. These depend, in turn, on the experimental volume-fixed mutual diffusion coefficients, chemical potential gradients, and volumetric data. Also required are the equivalent (electrical) conductances and ionic transference numbers. Values of the ℓ_{ij} are available for NaCl,[3] although they could be refined slightly by including more recent data for some of the input quantities.[7,58-61] However, due to a lack of published transference numbers for $SrCl_2$, we cannot calculate ℓ_{ij} for that salt, and, thus, we cannot test these promising approximation methods for $NaCl-SrCl_2-H_2O$ at this time.

A fourth and possibly useful (but perhaps less accurate) approach is to estimate the ternary main term thermodynamic diffusion coefficients L^{o}_{ii} from their corresponding limiting binary solution L^{o}. The cross term coefficient L^{o}_{12} (which equals L^{o}_{21}) could be estimated from the infinitely dilute solution approximation which is given as equation 73 of reference 4. From these estimated L^{o}_{ij}, the solvent fixed D^{o}_{ij} can be calculated by using[4]

$$D^{o}_{ij} = 1000 \sum_{k=1}^{2} L^{o}_{ik} \left(\frac{\partial \mu_{k3}}{\partial c_j}\right) \tag{10}$$

The volume fixed D_{ij} can then be obtained[4,9] from the equation

$$D_{ij} = \sum_{k=1}^{2} \left(\delta_{ki} - \frac{c_i \bar{V}_{k3}}{1000}\right) D^{o}_{kj} \qquad i,\ j = 1,2 \tag{11}$$

Here 1 and 2 denote Na^{+} and Sr^{2+}, respectively, 3 denotes Cl^{-}, δ_{ki} is the Kronecker delta, $\bar{V}_{k3}$ is the partial molal volume in $cm^3 \cdot mol^{-1}$ (given in Table I) of an electrolyte k3 whose cation is denoted by k, and μ_{k3} is the chemical potential of electrolyte k3.

Table X compares our experimental volume-fixed D_{ij} to two of the estimation procedures mentioned above: (1) the Nernst-Hartley limiting equation and (2) equating main term diffusion coefficients to their corresponding binary solution diffusion coefficients[7,58] at the total volumetric ionic strength of the mixtures (obtained graphically) with their cross terms set to zero. Several things should be noted:

(1) Both approximation methods predict values for D_{11} (the NaCl main term) that are too high, although the Nernst-Hartley method is slightly better. Errors range from +9 to +17% for the Nernst-Hartley values (average prediction error of +12%), and range from +9 to +29% for the binary solution approximation at the same ionic strength (average of +18.5%).

(2) For D_{22} (the $SrCl_2$ main term), neither method is obviously superior, although the binary solution approximation at the total ionic strength is slightly better. Both methods predict values of D_{22} that are too large. The Nernst-Hartley equations do better at $w_1=1/3$, but the binary solution approximation is better for D_{22} at $w_1=1/2$ and 2/3. Errors for the Nernst-Hartley equations range from +16 to +18% (average of +17%), and for the binary mixing approximation range from +6 to +24% (average of +14%).

(3) The Nernst-Hartley equations predict values of D_{12} that are too high in four cases, and too low in two others. Errors for the Nernst-Hartley equation range from -8 to +86% (average absolute error of +25%). The worst error is for $\bar{\bar{c}}_1+\bar{\bar{c}}_2=0.5$ mol•dm^{-3} and $w_1=1/3$; without it the average prediction error drops to 15%. The binary solution approximation at the total ionic strength has prediction errors of -100% since it incorrectly sets cross term $D_{ij}=0$ at all concentrations.

(4) The Nernst-Hartley equations predict values of D_{21} that are too high at $\bar{\bar{c}}_1+\bar{\bar{c}}_2=0.5$, but gives low predicted values at 1.0 mol•dm^{-3}. Errors at 0.5 mol•dm^{-3} range from +15 to +33% (average of +23%), but at 1.0 mol•dm^{-3} range from -1 to -10.5% (average of -7%). The binary solution approximation has prediction errors of -100%.

The Nernst-Hartley equation predicts values of D_{11} better than the binary solution approximation, whereas the opposite is true for D_{22}. However, the Nernst-Hartley equations must be considered the overall better approximation since they give cross-term D_{ij} that are in semi-quantitative agreement with experimental values, in contrast to the binary solution approximation which equates them to zero. It should be noted that for $\bar{\bar{c}}_1+\bar{\bar{c}}_2=1.0$ mol•dm^{-3} and $w_1=2/3$, the Nernst-Hartley equation predicts values of D_{12} and D_{21} that are nearly in exact agreement with experiment.

In general, neither of these methods yields particularly accurate results. The various other estimation procedures will be considered in more detail when additional ternary solution diffusion data become available.

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References

(1) Anderson, D. E.; Graf, D. L. Annual Review of Earth and Planetary Sciences 1976, 4, 95-121.

(2) Miller, D. G.; Ting, A. W.; Rard, J. A.; Eppstein, L. B. Geochim. Cosmochim. Acta, in press.

(3) Miller, D. G. J. Phys. Chem. 1966, 70, 2639-2659.

(4) Miller, D. G. J. Phys. Chem. 1967, 71, 616-632.

(5) Miller, D. G. J. Phys. Chem. 1981, 85, 1137-1146.

(6) Rard, J. A.; Miller, D. G. J. Solution Chem. 1979, 8, 755-766; 1983, 12, 413-425; 1985, 14, 271-299.

(7) Rard, J. A.; Miller, D. G. J. Solution Chem. 1979, 8, 701-716.

(8) Rard, J. A.; Miller, D. G. Z. Phys. Chem. N. F. 1984, 142, 141-155.

(9) Tyrrell, H. J. V.; Harris, K. R. "Diffusion in Liquids"; Butterworths: London, 1984.

(10) Dunlop, P. J.; Steele, B. J.; Lane, J. E. In "Physical Methods of Chemistry"; Weissberger, A., Rossiter, B. W., Eds.; Wiley: New York, 1972; Vol. 1, Chap. IV.

(11) Longsworth, L. G. In "The Structure of Electrolytic Solutions"; Hamer, W. J., Ed.; Wiley: New York, 1959; pp. 183-199.

(12) Vitagliano, V. Gazz. Chim. Ital. 1960, 90, 876-893, 1847-1858.

(13) Vitagliano, V.; Caramazza, R. Gazz. Chim. Ital. 1960, 90, 1730-1745.

(14) Albright, J. G.; Miller, D. G. J. Phys. Chem. 1972, 76, 1853-1857.

(15) O'Donnell, I. J.; Gosting, L. J. In "The Structure of Electrolyte Solutions"; Hamer, W. J., Ed.; Wiley: New York, 1959; pp 160-182.

(16) Dunlop, P. J. J. Phys. Chem. 1959, 63, 612-615.

(17) Kim, H. J. Chem. Eng. Data 1982, 27, 255-256.

(18) Fujita, H.; Gosting, L. J. J. Phys. Chem. 1960, 64, 1256-1263; recalculation of earlier data.

(19) Dunlop, P. J. Am. Chem. Soc. 1955, 77, 5238-5249.

(20) Dunlop, P. J. J. Phys. Chem. 1964, 68, 3062-3064; recalculation of earlier data.

(21) Fleming, R.; Johnson, J. R. J. Chem. Soc., Faraday Trans. 1 1981, 77, 849-858.

(22) Deshmukh, A. A., Fleming, R. In "Diffusion Processes"; Sherwood, J. N., Chadwick, A. V., Muir, W. M., Swinton, F. L., Eds.; Gordon and Breach: London, 1971; Vol. 1, pp 129-138.

(23) Kim, H. J. Solution Chem. 1974, 3, 149-159.

(24) Kim, H.; Deonier, R. C.; Reinfelds, G. J. Solution Chem. 1974, 3, 445-453.

(25) Revzin, A. J. Phys. Chem. 1972, 76, 3419-3429.

(26) Kim, H.; Reinfelds, G.; Gosting, L. J. J. Phys. Chem. 1973, 77, 934-940.

(27) Leaist, D. G.; Lyons, P. A. Aust. J. Chem. 1980, 33, 1869-1887.

(28) Jordan, M.; Kim, H. J. Solution Chem. 1982, 11, 347-355.

(29) Woolf, L. A.; Miller, D. G.; Gosting, L. J. J. Am. Chem. Soc. 1962, 84, 317-331.

(30) Woolf, L. A. J. Phys. Chem. 1963, 67, 273-277.

(31) Dunlop, P. J. J. Phys. Chem. 1965, 69, 4276-4283.

(32) Cussler, Jr., E. L.; Dunlop, P. J. J. Phys. Chem. 1966, 70, 1880-1888.

(33) Pepela, C. N.; Dunlop, P. J. J. Chem. Eng. Data 1972, 17, 207-208.

(34) Kim, H. J. Solution Chem. 1974, 3, 271-287.

(35) Sherrill, B. C.; Albright, J. G. J. Solution Chem. 1979, 8, 217-224.

(36) Wendt, R. P. J. Phys. Chem. 1962, 66, 1279-1288.

(37) Wiens, B.; Leaist, D. G. J. Chem. Soc., Faraday Trans. 1 1986, 82, 247-253.

(38) Edwards, O. W.; Dunn, R. L.; Hatfield, J. D.; Huffman, E. O.; Elmore, K. L. J. Phys. Chem. 1966 70, 217-226.

(39) Leaist, D. G. Can. J. Chem. 1985, 63, 2933-2939.

(40) Wendt, R. P.; Shamim, M. J. Phys. Chem. 1970, 74, 2770-2783.

(41) Wendt, R. P. J. Phys. Chem. 1965, 69, 1227-1237.

(42) Rard, J. A.; Miller, D. G. J. Chem. Eng. Data 1982, 27, 342-346.

(43) Rard, J. A.; Miller, D. G. J. Chem. Eng. Data, in press.

(44) Miller, D. G.; Rard, J. A.; Eppstein, L. B.; Albright, J. G. J. Phys. Chem. 1984, 88, 5739-5748; supplementary material.

(45) Rard, J. A.; Miller, D. G. J. Chem. Eng. Data 1984, 29, 151-156.

(46) Dunlop, P. J.; Gosting, L. J. J. Phys. Chem. 1959, 63, 86-93.

(47) Rard, J. A.; Miller, D. G., unpublished data.

(48) Miller, D. G.; Vitagliano, V.; Sartorio, R. J. Phys. Chem. 1986, 90, 1509-1519.

(49) Miller, D. G.; Vitagliano, V. J. Phys. Chem. 1986, 90, 1706-1717.

(50) Creeth, J. M. J. Am. Chem. Soc. 1955, 77, 6428-6440.

(51) Svensson, H. Optica Acta 1956, 3, 164-183.

(52) Creeth, J. M.; Gosting, L. J. J. Phys. Chem. 1958, 62, 58-65.

(53) Miller, D. G. J. Solution Chem. 1981, 10, 831-846.

(54) Albright, J. G.; Sherrill, B. C. J. Solution Chem. 1979, 8, 201-215.

(55) Fujita, H.; Gosting, L. J. J. Am. Chem. Soc. 1956, 78, 1099-1106.

(56) Robinson, R. A.; Stokes, R. H. "Electrolyte Solutions"; Butterworths: London, 1965.

(57) Weingärtner, H., private communication; Schönert, H., private communication.

(58) Rard, J. A.; Miller, D. G. J. Chem. Soc., Faraday Trans. 1 1982, 78, 887-896; 1983, 79, 1049 (errata).

(59) Della Monica, M.; Petrella, G.; Sacco, A.; Bufo, S. Electrochim. Acta 1979, 24, 1013-1017.

(60) Braun, B. M.; Weingärtner, H. J. Solution Chem. 1985, 14, 675-686.

(61) Panopoulos, D. K.; Kaneko, H.; Spiro, M. J. Solution Chem. 1986, 15, 243-252.

Table I. Parameters from Taylor Series Expansion of Densities About Mean Compositions[a]

c_1^*	c_2^*	d^*	H_1	H_2	$\sigma(d)$	$\bar{V}_1$	$\bar{V}_2$	$\bar{V}_0$
0.33333	0.16667	1.033236	0.039527	0.134714	1.3×10^{-5}	18.961	23.869	18.058
0.25000	0.25000	1.041160	0.039615	0.134732	1.7×10^{-5}	18.874	23.852	18.059
0.16667	0.33333	1.049093	0.039264	0.133477	2.2×10^{-5}	19.217	25.097	18.050
0.66667	0.33333	1.068492	0.038115	0.133541	1.0×10^{-5}	20.357	25.021	18.041
0.50000	0.50000	1.084144	0.038307	0.132578	2.0×10^{-5}	20.162	25.982	18.039
0.33333	0.66667	1.099730	0.038173	0.132175	2.1×10^{-5}	20.292	26.380	18.035

[a]Sub 1 denotes NaCl, sub 2 denotes $SrCl_2$, and sub 0 denotes H_2O. Units of c_i^* are $mol \cdot dm^{-3}$, of d^* and $\sigma(d)$ are $g \cdot cm^{-3}$, of H_i are $g \cdot dm^3 \cdot mol^{-1} \cdot cm^{-3}$, and of $\bar{V}_i$ are $cm^3 \cdot mol^{-1}$.

Table II. Concentrations and Total Fringe Numbers for 0.33315 mol•dm^{-3} NaCl-0.16662 mol•dm^{-3} $SrCl_2$-H_2O[a]

Experiment Number	1	2	3	4
$\bar{c}_1$	0.33314	0.33314	0.33316	0.33316
$\bar{c}_2$	0.16662	0.16662	0.16662	0.16662
Δc_1	+0.00002	+0.01887	+0.07557	+0.10015
Δc_2	+0.03438	+0.02673	+0.00669	0.00000
α_1	0.00021	0.19995	0.80006	0.99992
Δt	36.0	37.7	25.8	20.8
J_{exp}	87.51	84.70	85.06	90.07
J_{calc}	87.38	84.89	84.97	90.10

[a]Sub 1 denotes NaCl and sub 2 denotes $SrCl_2$. Units of $\bar{c}_i$ and Δc_i are mol•dm^{-3}, of Δt are s, and of J are fringes.

Table III. Concentrations and Total Fringe Numbers for 0.24987 mol•dm^{-3} NaCl-0.24993 mol•dm^{-3} $SrCl_2$-H_2O[a]

Experiment Number	1	2	3	4	5
$\bar{c}_1$	0.24986	0.24988	0.24985	0.24985	0.24990
$\bar{c}_2$	0.24993	0.24993	0.24995	0.24994	0.24991
Δc_1	+0.01893	+0.01896	+0.04740	+0.07584	+0.09675
Δc_2	+0.02685	+0.02684	+0.01677	+0.00673	+0.00004
α_1	0.20030	0.20061	0.50099	0.80006	0.99884
Δt	22.5	36.8	28.6	30.8	23.9
J_{exp}	84.78	84.66	84.68	84.98	86.80
J_{calc}	84.69	84.70	84.79	84.94	86.79

[a]Sub 1 denotes NaCl and sub 2 denotes $SrCl_2$. Units of $\bar{c}_i$ and Δc_i are are mol•dm^{-3}, of Δt and s, and of J are fringes.

Table IV. Concentrations and Total Fringe Numbers for 0.16657 $mol \cdot dm^{-3}$ NaCl-0.33325 $mol \cdot dm^{-3}$ $SrCl_2$-H_2O[a]

Experiment Number	1	2	3	4
$\bar{c}_1$	0.16657	0.16658	0.16658	0.16657
$\bar{c}_2$	0.33326	0.33326	0.33323	0.33326
Δc_1	+0.00002	+0.01907	+0.07635	+0.09545
Δc_2	+0.03327	+0.02659	+0.00668	-0.00001
α_1	0.00017	0.20206	0.80138	1.00018
Δt	37.9	28.3	37.4	28.9
J_{exp}	83.52	83.71	84.63	84.48
J_{calc}	83.57	83.68	84.47	84.61

[a]Sub 1 denotes NaCl and sub 2 denotes $SrCl_2$. Units of $\bar{c}_i$ and Δc_i are $mol \cdot dm^{-3}$, of Δt are s, and of J are fringes.

Table V. Concentration and Total Fringe Numbers for 0.66707 mol•dm^{-3} NaCl-0.33358 mol•dm^{-3} $SrCl_2$-H_2O[a]

Experiment Number	1	2	3	4
$\bar{c}_1$	0.66705	0.66707	0.66709	0.66709
$\bar{c}_2$	0.33356	0.33358	0.33361	0.33358
Δc_1	-0.00005	+0.01848	+0.07400	+0.09147
Δc_2	+0.03202	+0.02622	+0.00664	+0.00002
α_1	-0.00056	0.19941	0.79738	0.99951
Δt	38.1	37.9	24.4	31.1
J_{exp}	78.11	80.59	80.45	79.08
J_{calc}	78.42	80.25	80.35	79.23

[a]Sub 1 denotes NaCl and sub 2 denotes $SrCl_2$. Units of $\bar{c}_i$ and Δc_i are mol•dm^{-3}, of Δt are s, and of J are fringes.

Table VI. Concentrations and Total Fringe Numbers for 0.50053 mol•dm^{-3} NaCl-0.50052 mol•dm^{-3} $SrCl_2$-H_2O[a]

Experiment Number	1	2	3	4
$\bar{c}_1$	0.50056	0.50050	0.50055	0.50051
$\bar{c}_2$	0.50054	0.50052	0.50051	0.50051
Δc_1	+0.00001	+0.01859	+0.07480	+0.09426
Δc_2	+0.03325	+0.02650	+0.00658	+0.00008
α_1	0.00013	0.19742	0.79946	0.99768
Δt	31.0	34.7	28.9	26.2
J_{exp}	81.38	80.38	80.19	80.87
J_{calc}	81.20	80.62	80.11	80.90

[a]Sub 1 denotes NaCl and sub 2 denotes $SrCl_2$. Units of $\bar{c}_i$ and Δc_i are mol•dm^{-3}, of Δt are s, and of J are fringes.

Table VII. Concentrations and Total Fringe Numbers for 0.33331 mol•dm^{-3} NaCl-0.66666 mol•dm^{-3} $SrCl_2$-H_2O[a]

Experiment Number	1	2	3	4
$\bar{c}_1$	0.33332	0.33330	0.33330	0.33332
$\bar{c}_2$	0.66670	0.66666	0.66662	0.66666
Δc_1	0.00000	+0.01697	+0.07575	+0.09528
Δc_2	+0.03306	+0.02621	+0.00648	+0.00001
α_1	-0.00000_4	0.18441	0.80342	0.99979
Δt	39.0	34.9	30.8	23.0
J_{exp}	80.36	78.25	80.09	80.98
J_{calc}	80.42	78.17	80.12	80.98

[a]Sub 1 denotes NaCl and sub 2 denotes $SrCl_2$. Units of $\bar{c}_i$ and Δc_i are mol•dm^{-3}, of Δt are s, and of J are fringes.

Table VIII. Diffusion Coefficients and Refractometric Data at $\bar{\bar{c}}_1+\bar{\bar{c}}_2=0.5$ mol•dm^{-3} [a]

$\bar{\bar{c}}_1$	0.33315	0.24987	0.16657
$\bar{\bar{c}}_2$	0.16662	0.24993	0.33325
$\bar{\bar{c}}_0$	54.806	54.782	54.760
$m_1(\bar{\bar{c}}_1,\bar{\bar{c}}_2)$	0.33742	0.25318	0.16885
$m_2(\bar{\bar{c}}_1,\bar{\bar{c}}_2)$	0.16876	0.25324	0.33781
R_1	899.60	896.05	886.60
R_2	2540.92	2522.78	2511.31
s_+	267.54	271.83	278.31
s_-	337.98	329.01	315.39
S_A	-62.79	-60.79	-60.00
$10^5 x D_{11}$	1.3502±0.0068	1.2935±0.0154	1.2454±0.0689
$10^5 x D_{12}$	0.3721±0.0030	0.2603±0.0034	0.1022±0.0029
$10^5 x D_{21}$	0.0598±0.0003	0.0850±0.0007	0.1073±0.0034
$10^5 x D_{22}$	0.9223±0.0068	0.9836±0.0154	1.0510±0.0643
$10^5 x D^{\circ}_{11}$	1.3593	1.3002	1.2499
$10^5 x D^{\circ}_{12}$	0.3819	0.2675	0.1070
$10^5 x D^{\circ}_{21}$	0.0644	0.0917	0.1163
$10^5 x D^{\circ}_{22}$	0.9272	0.9908	1.0606

[a]Units of c_i are mol•dm^{-3}, of m_i are mol•kg^{-1}, of R_i are fringes•dm^3•mol^{-1}, of s_+ and s_- are cm^{-1}•s$^{1/2}$, and of D_{ij} are cm^2•s^{-1}. Sub 1 denotes NaCl, sub 2 $SrCl_2$, and sub 0 H_2O.

Table IX. Diffusion Coefficients and Refractometric Data at $\bar{\bar{c}}_1+\bar{\bar{c}}_2=1.0$ $mol \cdot dm^{-3}$ [a]

$\bar{\bar{c}}_1$	0.66707	0.50053	0.33331
$\bar{\bar{c}}_2$	0.33358	0.50052	0.66666
$\bar{\bar{c}}_0$	54.207	54.157	54.097
$m_1(\bar{\bar{c}}_1,\bar{\bar{c}}_2)$	0.68300	0.51303	0.34201
$m_2(\bar{\bar{c}}_1,\bar{\bar{c}}_2)$	0.34155	0.51302	0.68406
R_1	865.81	856.20	849.71
R_2	2450.47	2441.81	2432.68
s_+	268.50	274.03	277.39
s_-	346.63	333.88	325.95
S_A	-63.68	-62.56	-62.02
$10^5 \times D_{11}$	1.3068±0.0065	1.2302±0.0108	1.1860±0.0401
$10^5 \times D_{12}$	0.4765±0.0036	0.2956±0.0022	0.2007±0.0035
$10^5 \times D_{21}$	0.0800±0.0005	0.1144±0.0007	0.1385±0.0031
$10^5 \times D_{22}$	0.9127±0.0072	0.9986±0.0119	1.0548±0.0430
$10^5 \times D^{\circ}_{11}$	1.3263	1.2444	1.1955
$10^5 \times D^{\circ}_{12}$	0.4987	0.3120	0.2116
$10^5 \times D^{\circ}_{21}$	0.0898	0.1286	0.1574
$10^5 \times D^{\circ}_{22}$	0.9238	1.0150	1.0766

[a] Units of c_i are $mol \cdot dm^{-3}$, of m_i are $mol \cdot kg^{-1}$, of R_i are fringes$\cdot dm^3 \cdot mol^{-1}$, of s_+ and s_- are $cm^{-1} \cdot s^{1/2}$, and of D_{ij} are $cm^2 \cdot s^{-1}$. Sub 1 denotes NaCl, sub 2 $SrCl_2$, and sub 0 H_2O.

Table X. Comparison of Experimental D_{ij} to Simple Estimates for $NaCl-SrCl_2-H_2O$

	$\bar{\bar{c}}_1$=0.33315 $\bar{\bar{c}}_2$=0.16662	$\bar{\bar{c}}_1$=0.24987 $\bar{\bar{c}}_2$=0.24993	$\bar{\bar{c}}_1$=0.16657 $\bar{\bar{c}}_2$=0.33325	$\bar{\bar{c}}_1$=0.66707 $\bar{\bar{c}}_2$=0.33358	$\bar{\bar{c}}_1$=0.50053 $\bar{\bar{c}}_2$=0.50052	$\bar{\bar{c}}_1$=0.33331 $\bar{\bar{c}}_2$=0.66666
			Experimental			
$10^5 \times D_{11}$	1.3502	1.2935	1.2454	1.3068	1.2302	1.1860
$10^5 \times D_{12}$	0.3721	0.2603	0.1022	0.4765	0.2956	0.2007
$10^5 \times D_{21}$	0.0598	0.0850	0.1073	0.0800	0.1144	0.1385
$10^5 \times D_{22}$	0.9223	0.9836	1.0510	0.9127	0.9986	1.0548
			Nernst-Hartley			
$10^5 \times D_{11}$	1.467	1.422	1.386	1.467	1.422	1.386
$10^5 \times D_{12}$	0.474	0.312	0.186	0.474	0.312	0.186
$10^5 \times D_{21}$	0.079	0.104	0.124	0.079	0.104	0.124
$10^5 \times D_{22}$	1.073	1.162	1.232	1.073	1.162	1.232
			Binary D_{ij} Estimates			
$10^5 \times D_{11}$	1.478	1.482	1.48[illegible]	1.503	1.516	1.530
$10^5 \times D_{12}$	0.0	0.0	0.0	0.0	0.0	0.0
$10^5 \times D_{21}$	0.0	0.0	0.0	0.0	0.0	0.0
$10^5 \times D_{22}$	1.110	1.112	1.115	1.127	1.137	1.146

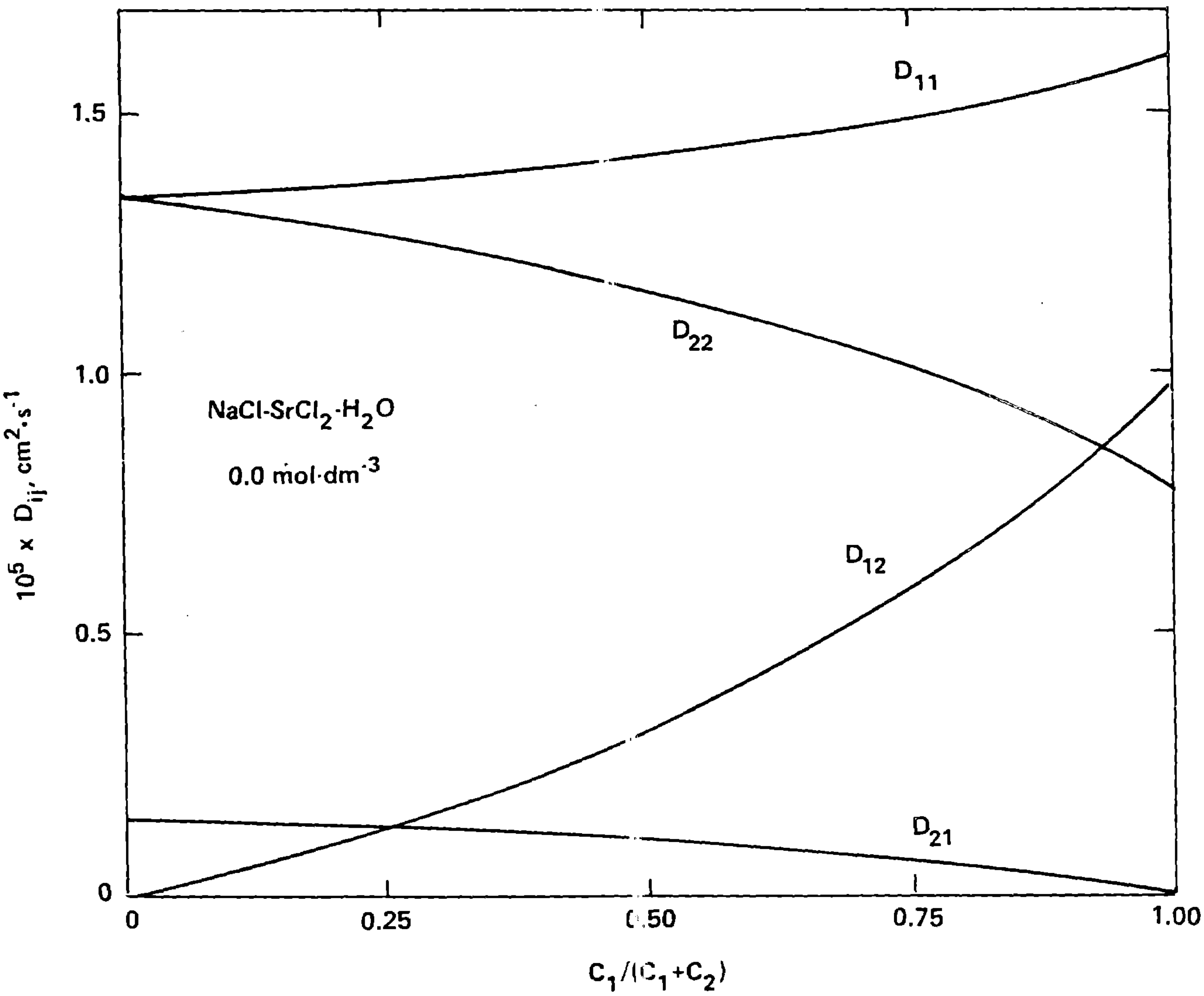
[a]Units of $\bar{c}_i$ are $mol \cdot dm^{-3}$ and of D_{ij} are $cm^2 \cdot s^{-1}$. Binary D_{ij} estimates are made for the total ionic strength of the mixture.

Figure Captions

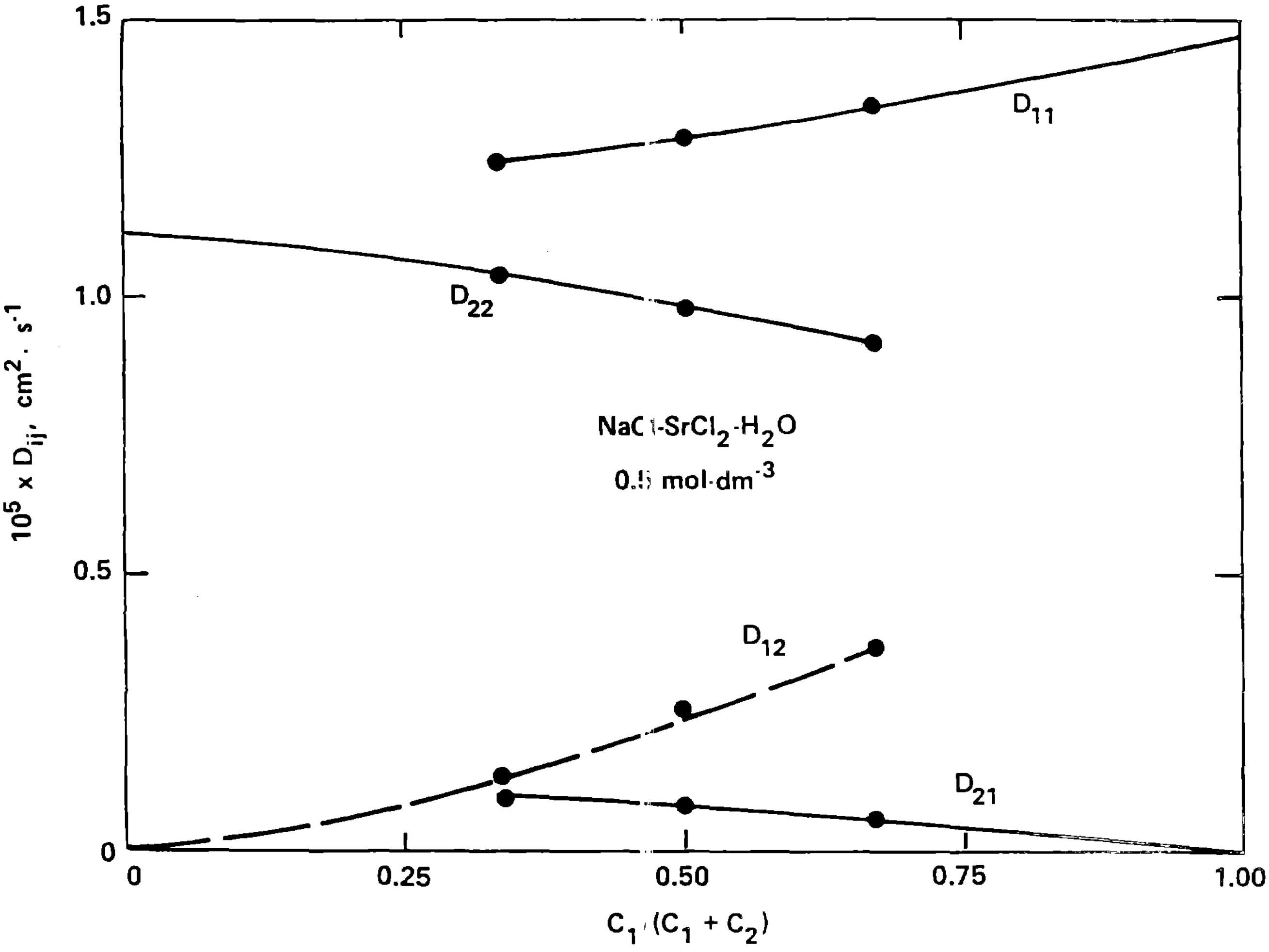
Figure 1. Mutual diffusion coefficients of $NaCl-SrCl_2-H_2O$ at 25°C and infinite dilution as a function of the molarity fraction of NaCl, calculated from the Nernst-Hartley equations. NaCl is denoted by 1 and $SrCl_2$ by 2.

Figure 2. Experimental mutual diffusion coefficients of $NaCl-SrCl_2-H_2O$ at 25°C and a total molarity of 0.5 $mol \cdot dm^{-3}$. NaCl is denoted by 1 and $SrCl_2$ by 2.

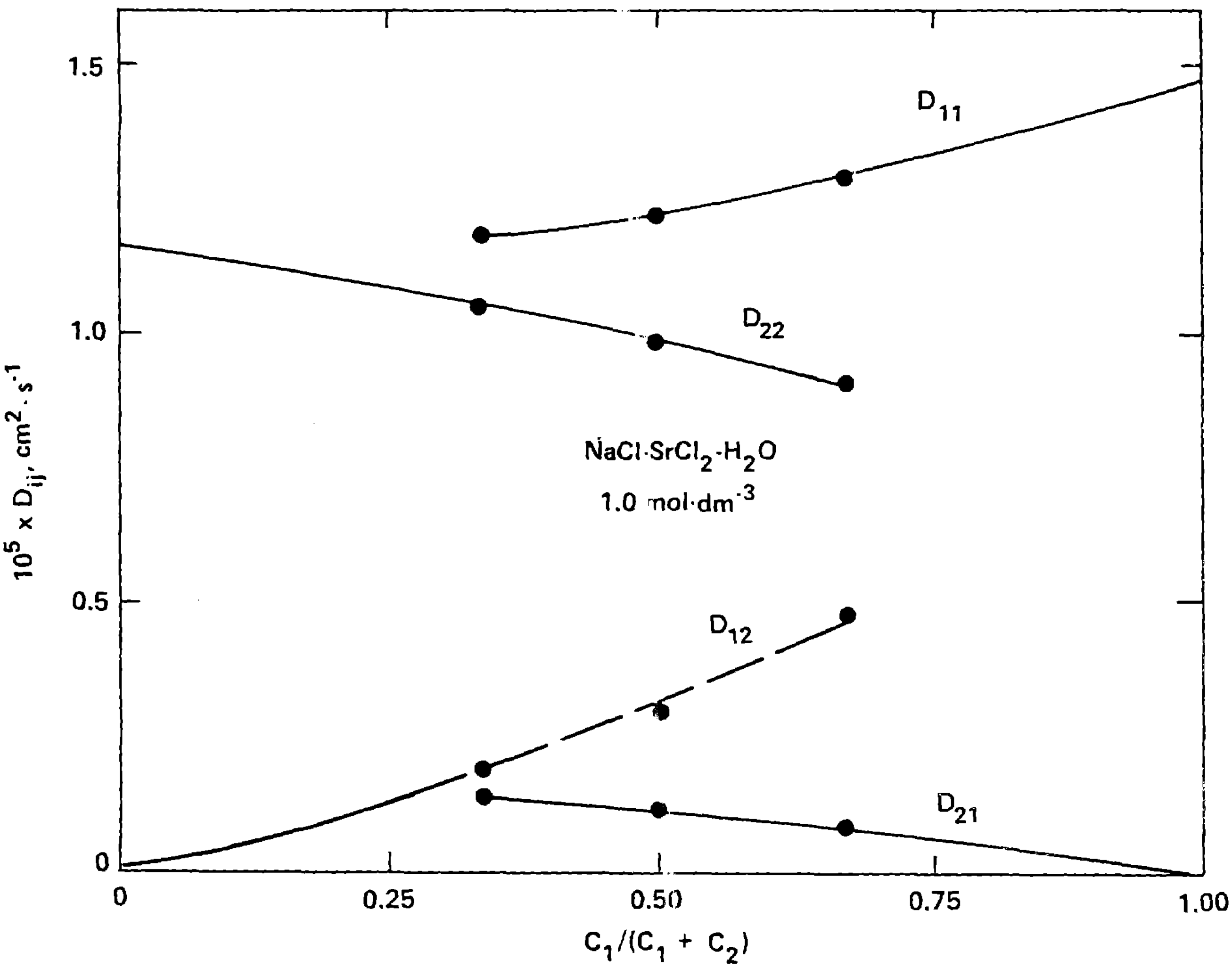
Figure 3. Experimental mutual diffusion coefficients of $NaCl-SrCl_2-H_2O$ at 25°C and a total molarity of 1.0 $mol \cdot dm^{-3}$. NaCl is denoted by 1 and $SrCl_2$ by 2.



D_{11}
D_{22}
D_{12}
D_{21}
NaCl-SrCl$_2$-H$_2$O
0.0 mol·dm^{-3}
$10^5 \times D_{ij}$, cm^2·s^{-1}
1.5
1.0
0.5
0
0.25
0.50
0.75
1.00
$C_1/(C_1+C_2)$



1.5
1.0
0.5
0
$10^5 \times D_{ij}$, $cm^2 \cdot s^{-1}$
D_{11}
D_{22}
$NaCl$-$SrCl_2$-H_2O
0.5 mol·dm^{-3}
D_{12}
D_{21}
0
0.25
0.50
0.75
1.00
$C_1/(C_1 + C_2)$



1.5
1.0
0.5
0
0
0.25
0.50
0.75
1.00
$10^5 \times D_{ij}$, $cm^2 \cdot s^{-1}$
$C_1/(C_1 + C_2)$
D_{11}
D_{22}
D_{12}
D_{21}
$NaCl \cdot SrCl_2 \cdot H_2O$
1.0 mol·dm^{-3}